

Polarized Wannier functions: *ab-initio* study of the dielectric properties of silicon and gallium arsenide

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We present a first-principles calculation of the electronic properties of crystalline silicon and gallium arsenide in a uniform electric field. Polarized Wannier-like functions which are confined in a finite region are obtained by minimizing a total-energy functional which depends explicitly on the macroscopic polarization of the solid. The polarization charge density and the electronic dielectric constant are computed via finite differences. The results coincide with those of the linear response approach in the limit of vanishing electric field and infinite localization region.

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The study of materials in a finite electric field is a difficult theoretical problem which is not definitively settled yet [1]. The main difficulty is that the scalar potential which describes the field is not periodic and is not bounded from below: crystal momentum is no longer a good quantum number and no ground state exists for the electrons of the solid. *Ab-initio* studies of the response of crystals to uniform electric fields have been done mainly with linear response theory (LRT). Dielectric constants [2], piezoelectric tensors [3], second order non-linear susceptibilities [4], and Born effective charges [2] of several materials have been computed with density functional perturbation theory (DFPT) [2,5]. In practice however with these methods only the response to *infinitesimal* electric fields can be studied.

A major issue is therefore the study of solids in a *finite* electric field. Linear as well as nonlinear susceptibilities could be extracted simultaneously from such calculations, together with important informations on technologically interesting phenomena, such as electromigration, which have eluded, until now, a detailed *ab-initio* investigation [6]. Only a few direct calculations with finite electric fields have been done with large supercells and artificially periodic fields [7,8]. Recently Nunes and Vanderbilt [9] have proposed an approach to circumvent the difficulties associated with finite electric fields: they have shown that localized Wannier functions (LWFs) allow one to write a functional for the energy of a solid in a uniform electric field. The ground state of this functional corresponds to a meta-stable state for the real solid [10], but, in the limit of vanishing electric field, the derivatives of the functional provide the same dielectric properties (polarization, linear [9] and non-linear [4] dielectric constants) as the perturbative approach. The method has so far been applied only to a simple one-dimensional tight-binding model. In this Letter we demonstrate its applicability within a self-consistent scheme by computing the dielectric properties of silicon and gallium arsenide. This

study is of relevance also for ‘order N’ electronic structure calculations [11] since LWFs are a key-ingredient for many of these methods.

In a previous work [12], we computed LWFs of silicon and gallium arsenide in zero electric field within a self-consistent scheme in the local density approximation (LDA). In this work, we consider these two materials in a finite electric field and obtain their *polarized* WFs. We study the ability of the latter to predict the electronic properties of insulators in a uniform electric field and discuss the convergence of the dielectric properties with increasing size of the localization region (LR).

As underlined by Gonze, Ghosez, and Godby [13] the validity of the Hohenberg and Kohn theorem [14] for an infinite insulating crystal in a macroscopic electric field is questionable and in principle one should add the macroscopic polarization as a basic variable. Martin and Ortiz [1] have recently reformulated the DFT for insulating crystals to include electric field effects. However, no realistic polarization-dependent functional has been proposed yet and in this work we remain at the standard LDA level. We use equations similar to those of Ref. [1] except for the “exchange and correlation field”, which stems from the polarization dependence of the exchange and correlation energy.

We describe first how to implement finite electric fields in our scheme [12] based on LWFs. We then show that the variation of the charge density induced, at first order, by a finite electric field, and computed with polarized LWFs, converges to the values provided by LRT. We also analyze the induced macroscopic polarization and show that, increasing the size of the LRs, its derivative with respect to the field converges exponentially. The asymptotic values, for vanishing field, are close to the DFPT results. Finally we present examples of polarized WFs.

The electronic ground state of a periodic crystal containing N interacting electrons can be described either by $N/2$ independent Bloch orbitals or by $N/2$ WFs. One

way to obtain approximate WFs for solids has been presented in Ref. [11] and implemented in a self-consistent DFT scheme in our previous work [12]. The method is based on the minimization of a total energy functional $E_{tot}[\{|v_{0,n}\rangle\}]$ which includes implicitly orthogonalization constraints with respect to $M = N_e/2$ localized orbitals $\{|v_{0,n}\rangle\}$, where N_e is the number of electrons per unit cell, $n = 1, \dots, M$ is the band index, and the subscript 0 indicates that the orbital is centered in the unit cell containing the origin. The periodicity of the crystal is exploited by requiring that the remaining orbitals are obtained by translating those of the first cell by all the Bravais lattice vectors \mathbf{R}_l : $|v_{l,n}\rangle = \hat{T}_{\mathbf{R}_l}|v_{0,n}\rangle$.

As already mentioned, the Hamiltonian of an infinite, periodic crystal in presence of a uniform static electric field \mathbf{E} [15], is not bounded from below. However if the degrees of freedom $\{|v_{0,n}^{\mathbf{E}}\rangle\}$ are constrained to be localized in finite regions and the electric field is sufficiently small, the functional [9]

$$F[\{|v_{0,n}^{\mathbf{E}}\rangle\}] = E_{tot}[\{|v_{0,n}^{\mathbf{E}}\rangle\}] - \Omega \mathbf{P} \cdot \mathbf{E}, \quad (1)$$

(where Ω is the unit-cell volume and the macroscopic electric polarization \mathbf{P} is the sum of the electronic \mathbf{P}_e and ionic contributions) has a well defined minimum which represents a meta-stable state for the real solid [9,10]. In the limit where the size of the LRs becomes infinite, the maximum allowed field goes to zero. For any non-vanishing value of the electric field \mathbf{E} , the second term in Eq. (1) will cause a change in the periodic density and also a variation of the macroscopic polarization. In our calculations, the value of the screened electric field \mathbf{E} is kept fixed, while the macroscopic polarization changes self-consistently. Physically we compute variations of the charge density, of the macroscopic polarization, and of the total energy with respect to the screened uniform electric field instead of the bare external electric field \mathbf{E}_0 .

At zero field, the functional is minimized by almost orthogonal orbitals which, for sufficiently large LRs, are a good approximation to a set of WFs $\{|w_{0,n}\rangle\}$ of the solid. Similar sets of WFs can also be obtained through a unitary transformation of the Bloch orbitals with an appropriate choice of the phases [16]. In presence of a finite field, the functions $\{|v_{0,n}^{\mathbf{E}}\rangle\}$ which minimize the functional are still approximately orthogonal and, for large LRs, approximate a set of *polarized* WFs for the solid. The electronic contribution \mathbf{P}_e to the macroscopic polarization \mathbf{P} can be related [17] to the *centers* $\mathbf{r}_n = \langle w_{0,n} | \mathbf{r} | w_{0,n} \rangle$ of the WFs of the system by $\Omega \mathbf{P}_e = -2e \sum_{n=1}^M \mathbf{r}_n$. This definition can be extended to non-zero values of the screened macroscopic electric field and to LWFs by [9]:

$$\Omega \mathbf{P}_e[\{|v_{0,n}^{\mathbf{E}}\rangle\}, \mathbf{E}] = -2e \sum_{n=1}^M \mathbf{r}_n(\mathbf{E}), \quad (2)$$

with $\mathbf{r}_n(\mathbf{E})$ given by

$$\mathbf{r}_n(\mathbf{E}) = \sum_l \sum_{m=1}^M \langle v_{0,n}^{\mathbf{E}} | \mathbf{r} | v_{l,m}^{\mathbf{E}} \rangle Q_{m,n}^{l,0}(\mathbf{E}), \quad (3)$$

where e is the electronic charge, and $Q_{m,n}^{l,0}(\mathbf{E}) = 2\delta_{l,0}\delta_{m,n} - \langle v_{l,m}^{\mathbf{E}} | v_{0,n}^{\mathbf{E}} \rangle$ is the first-order approximation to the inverse of the overlap matrix between LWFs.

This extended definition of \mathbf{P}_e allows one to study the dielectric properties of insulating crystals in finite electric fields. The validity of this definition rests on the agreement of the values of the dielectric properties computed in the limit of vanishing field with the LRT results [9,4]. In this limit the equivalence between the two methods can be demonstrated analytically. The electronic dielectric tensor $\epsilon_{\alpha\beta}^{\infty}(\mathbf{E})$ is related to the macroscopic electronic polarization \mathbf{P}_e by

$$\epsilon_{\alpha\beta}^{\infty}(\mathbf{E}) = \delta_{\alpha\beta} + 4\pi \frac{dP_{e,\alpha}(\mathbf{E})}{dE^{\beta}} \quad (4)$$

where α and β indicate Cartesian coordinates. It can be obtained by finite differences of the macroscopic polarization $\mathbf{P}_e(\mathbf{E})$ for different values of the screened electric field \mathbf{E} . $\mathbf{P}_e(\mathbf{E})$ refers to $\mathbf{P}_e[\{|v_{0,n}^{\mathbf{E}}\rangle\}, \mathbf{E}]$ of Eq. (2) computed for the orbitals $\{|v_{0,n}^{\mathbf{E}}\rangle\}$ which correspond, for a given electric field \mathbf{E} , to the minimum of the functional F .

The search for the minimum of the total-energy functional F requires its functional derivative with respect to the variational degrees of freedom $\langle \mathbf{r} | v_{0,n}^{\mathbf{E}} \rangle$. Differentiating Eq. (1) with respect to $\langle \mathbf{r} | v_{0,n}^{\mathbf{E}} \rangle$, the polarization term gives an additional contribution with respect to the zero-field case, which can be recast as:

$$4 \sum_{l,m} \left[\hat{T}_{\mathbf{R}_l}(\mathbf{r} | v_{0,m}^{\mathbf{E}} \rangle) Q_{m,n}^{l,0} - |v_{l,m}^{\mathbf{E}}\rangle \langle v_{l,m}^{\mathbf{E}} | \mathbf{r} | v_{0,n}^{\mathbf{E}} \rangle \right] \cdot e \mathbf{E}. \quad (5)$$

The LWFs have been represented on a uniform real-space mesh and $\langle \mathbf{r} | v_{0,n}^{\mathbf{E}} \rangle$ is allowed to be non-zero only inside cubic regions with size $2a_{LR}$. As in the zero-field case, the localization of the LWFs makes the summations in Eqs. (3) and (5) finite. The periodic valence charge density $n(\mathbf{r}; \mathbf{E})$ (whose expression is the same as in the zero-field case) is a sum of localized contributions. The Fourier components $\tilde{n}(\mathbf{G}; \mathbf{E})$ allow us to compute the Coulomb electrostatic energy per unit cell as $E_H = \frac{\Omega}{2} \sum_{\mathbf{G} \neq 0} \tilde{n}^*(\mathbf{G}; \mathbf{E}) \tilde{V}_H(\mathbf{G}; \mathbf{E})$, where $\tilde{V}_H(\mathbf{G}; \mathbf{E})$ is the Fourier transform of the Hartree potential. The $\mathbf{G} = 0$ component of the Hartree potential is included in the screened electric field \mathbf{E} and it is not explicitly evaluated.

We have applied this approach to crystalline silicon and gallium arsenide. The unit cell contains 2 atoms and the electronic ground-state can be described by $M = 4$ LWFs which are confined within LRs centered on the four bonds in the unit cell at the origin. Our calculations have been carried out within DFT-LDA [18] and with norm-conserving pseudopotentials in the Kleinman-Bylander

form [19]. All technical details and parameters are the same as those given in Ref. [12].

In Fig. 1, we show the charge density induced by a field in the [100] direction and with an intensity equal to $e|\mathbf{E}| = 10^{-3}$ a.u. $\approx 5.14 \times 10^8$ V/m. The induced valence charge density $\Delta n(\mathbf{r}) = n(\mathbf{r}; \mathbf{E}) - n(\mathbf{r}, \mathbf{0})$ computed with LWFs obtained for different values of a_{LR} is compared in Fig. 1(a) with the result of the conventional linear response approach [2] $n^{(1)}(\mathbf{r}) = \mathbf{E} \frac{\partial n(\mathbf{r})}{\partial \mathbf{E}} \Big|_{\mathbf{E}=0}$ obtained using a Bloch orbital representation of the electronic wave-functions [20]. The weak intensity of the field ensures a linear behaviour for both silicon and gallium arsenide. Fig. 1(a) shows that all the features of the charge density linearly induced by the field are correctly reproduced with small LRs. Localization regions containing 216 atoms ($a_{LR}/a = 34/24$) are large enough to obtain an induced charge density which is practically undistinguishable from the LRT result on the scale of the figure. The difference is everywhere less than 4.7×10^{-3} e/cell for silicon and 6.1×10^{-3} e/cell for gallium arsenide. In the case of gallium arsenide, this error is smaller than that associated with the use of a semi-local pseudopotential instead of the Kleinman-Bylander form used here.

In Fig. 2, we display the values of the high-frequency-dielectric constants of silicon and gallium arsenide computed with our method at $\mathbf{E} = \mathbf{0}$ for different sizes of the LRs. Fitting the data with an exponential function $\epsilon^\infty = A \exp(-(a_{LR}/a)/\alpha) + B$, we obtain in the limit $a_{LR} \rightarrow \infty$ the values $B = 13.4 \pm 0.2$ for silicon and $B = 11.6 \pm 0.1$ for gallium arsenide. The LRT results are 12.9 and 11.4 respectively, thus, supporting the use of LWFs in the study of the dielectric properties of solids. The convergence of the dielectric constant with increasing values of a_{LR} is slower than that of structural properties [12]. The exponential fitting curves correspond to the parameters: $A = -13.2 \pm 0.3$, $\alpha = 0.81 \pm 0.05$ for silicon and $A = -10.4 \pm 0.2$, $\alpha = 0.83 \pm 0.05$ for gallium arsenide. For the largest localization size considered ($a_{LR}/a = 2$ which contains 512 atoms) we obtain $\epsilon^\infty = 12.3$ for silicon and $\epsilon^\infty = 10.6$ for gallium arsenide, which underestimate the LRT results by 5% and 7% respectively.

In Fig. 3(a), we show the polarized LWF computed at the theoretical lattice constant, $a_{LR}/a = 34/24$, and with an electric field $e|\mathbf{E}| = 10^{-3}$ Ha/a.u. in the [100] direction for silicon and gallium arsenide. The electric field displaces the center of each LWF with respect to the zero-field case, as indicated with arrows in Fig. 3(b). By summing over the four functions within the unit cell at the origin, the individual displacements perpendicular to the field cancel out and the induced macroscopic polarization is parallel to the field, as expected for solids with cubic symmetry.

In conclusion we have shown that LWFs, a key ingredient of several ‘order N’ methods for electronic structure

calculations, also allow one to study solids in presence of a finite electric field. The induced charge density and the dielectric constant obtained from finite differences converge, in the limit of large LRs and small electric fields, towards the LRT values. Furthermore a first example of approximate, *polarized* WFs has been provided.

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sampling of the irreducible Brillouin zone to compute the first-order variation of the valence charge density due to the electric field.

FIG. 1. Valence charge density $\Delta n(\mathbf{r})$ (in units of e/cell) induced by a macroscopic electric field \mathbf{E} in the [100] direction (with $e|\mathbf{E}| = 10^{-3}$ a.u.). Panel (a): Comparison of results obtained for two different values of a_{LR}/a (the number of atoms inside a LR is in square brackets) with the LRT result. The induced density is represented along the [111] direction at the theoretical unit cell volume and $d = \sqrt{3}a$. Panel (b): Contour-plots in the (0̄11) plane of $\Delta n(\mathbf{r})$ for the largest LR size. The contours are drawn at constant intervals of 0.02 e/cell. The thicker contour denotes $\Delta n(\mathbf{r}) = 0$, the continuous (dashed) contours are for $\Delta n(\mathbf{r}) > 0$ ($\Delta n(\mathbf{r}) < 0$).

FIG. 2. Linear dielectric constant ϵ^∞ of silicon and gallium arsenide computed with LWFs using different LR sizes. The values of ϵ^∞ for $a_{LR} \rightarrow \infty$ are obtained by numerical extrapolation. ϵ_{LRT}^∞ indicates the LRT value. Calculations have been performed at the theoretical lattice constants [12]: $a_0 = 10.20$ a.u. for silicon and $a_0 = 10.48$ a.u. for gallium arsenide.

FIG. 3. Panel (a): Contour-plots in the (0̄11) plane of the polarized LWFs in a.u. obtained for an electric field $e|\mathbf{E}| = 10^{-3}$ a.u. oriented along [100]. These polarized LWFs are constrained to be zero outside a LR with size $a_{LR}/a = 34/24$ and centered on the bond oriented along the [111] direction. The contour intervals are 0.01 a.u. for negative values (dashed lines) and 0.1 a.u. for positive values (continuous lines). Panel (b): Contour-plots of the variation of the LWFs $\langle \mathbf{r} | \Delta v_{0,n=1} \rangle = \langle \mathbf{r} | v_{0,n=1}^{\mathbf{E}} \rangle - \langle \mathbf{r} | v_{0,n=1}^{\mathbf{E}=\mathbf{0}} \rangle$. The contour interval is 10^{-3} a.u. for silicon and 2×10^{-4} a.u. for gallium arsenide. The LWF centers are indicated by empty circles while their variation is depicted by arrows whose length has been magnified by a factor 100.

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